# RIM-FORMING DOLOMITIC AGGREGATE IN CONCRETE STRUCTURES IN SAUDI ARABIA - IS DEDOLOMITIZATION EQUAL TO THE SO-CALLED ALKALI-CARBONATE REACTION ?

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#### Abstract

A highly chemically reactive dolomitic aggregate used for PC wall structures, later cracked and debonded around reinforcing steel bars, developed conspicuous rim due to dedolomitization without forming expansion cracks around the aggregate. Contents of cement alkali (Na<sub>2</sub>Oeq 0.62%) and cryptocrystalline quartz in the aggregate (1.0%) were too small to cause ASR in natural conditions, except for a harmless pozzolanic reaction. Accelerated RILEM tests (AAR-2, AAR-5) indicated that the aggregate was neither deleteriously expansive due to ASR nor ACR. Petrographic examination revealed that the concrete failure was associated with the use of unwashed aggregate, inappropriate removal of concrete forms, and poor workmanship in the casting and repair work.

Keywords: alkali-budgets, alkali-carbonate reaction, dedolomitization, debonding, minimum cement alkali

# **1 INTRODUCTION**

During the construction of pre-stressed concrete wall structures, initial defects and poor performances of repaired concrete were noted within 6 months after casting concrete, including cold joints, vertical and horizontal cracks, debonding of concrete cover, and delamination of repaired mortars. Because rim-formation was conspicuous on the dolomitic limestone coarse aggregate, there was a concern about deleteriously expansive alkali-carbonate reaction (ACR). Hence, to identify the cause of the deterioration, detailed petrographic examinations were made of concrete core specimens taken, along with accelerated expansion tests of the aggregate and concrete, to examine their potential alkali reactivity and reaction products of ASR and ACR. Evidence of reaction and expansion was strictly distinguished in the petrographic examination, following the work on ACR [1].

#### 2 MATERIALS AND METHODS

Concrete core specimens (dia.45mm-dia.70mm x L200mm) were taken from 5 structures (K1, K2, K4, C1 and C4), including sound, cracked and repaired portions. Type 1 Portland cement and clinker from the same source (6 month later) were obtained for comparison, along with aggregates in the stockpile. Before thin sectioning, concrete cores were subjected to core-scanning (360° continuous image) and stereomicroscopy to record outer textures. Polished thin sections (30mm by 20mm, thickness 15µm) were examined by polarizing microscopy, then subjected to quantitative EDS analysis (JEOL JSM 5310LV/JED 2140: 15KV, 0.12nA) to identify reaction products (sound and cracked areas), as well as to estimate minimum alkali content of the cement used, based on unhydrated cement particles in concrete (sound areas)[2]. Wet chemical analyses were also made of cement and clinker for bulk composition; water-soluble alkali of concrete and aggregates [3]; and phosphoric acid treatment of coarse aggregate to determine the amount of free-silica. RILEM AAR-2 and 5 tests (80°C, 1M NaOH) of coarse aggregate, and an accelerated concrete core expansion test under the same accelerating condition (dia.45mm x L130mm)[2], were conducted to evaluate potential alkali reactivity of the aggregate (sound and cracked portions).

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## 3 RESULTS

## 3.1 Coarse aggregate

The crushed coarse aggregate in the stockyard from the local quarry is dolimitic limestone. The above contained less than 1% of free-silica, as determined by the phosphoric acid treatment (Table 1).

## 3.2 Cement

#### Setting time of the cement

The Portland cement obtained half a year later contained small alkali (Na<sub>2</sub>Oeq) of 0.62%, nearly low-alkali cement, and over 3% of CO<sub>2</sub> and MgO, suggestive of the addition of dolomitic limestone powder (about 10%) (Table 2). The average dilution ratios of cement/clinker estimated for SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> was 0.86, which (as 0.85) will be used as a conversion factor of alkali content from clinker to cement. Cement clinker contained much amount of free-lime (f.CaO). The final setting time (ASTM C191 01a) of the cement tested was normal (23°C, 3 hours and 30 minutes), but neat paste presented some viscose stiffening, not a false set, suggesting that the cement might have slightly low workability. The presence of free-lime in excess of 1% may be responsible for this nature.

#### Cement clinker and water-soluble alkali

The cement clinker contained moderate level of alkali (0.74% Na<sub>2</sub>Oeq) but much free-lime (2.7% f.CaO). The phase composition calculated after Bogue's norm gave: alite 51.8%, belite 19.8%, aluminate 8.6% and ferrite 11.7% regarding the free lime content, or, alite 62.8% and belite 11.4% ignoring this. SEM-EDS analysis identified arcanite (K<sub>2</sub>SO<sub>4</sub>) to be the main alkali sulfate phase in clinker, with potential content 1.2% (Table 2, Figure 4h). The aluminate phase was mainly of the cubic variety with limited amount of incorporated alkali (Figure 4g). The minimum alkali content of clinker, omitting water-soluble alkali from the sulfate, ranged Na<sub>2</sub>Oeq 0.3-0.4% (Table 4). To estimate the total alkali content in the original clinker used, a conversion factor (the ratio of the total alkali versus non-sulfate alkali in cement) was sought (Table 3). This figure (2.07, rounded as 2.0) will be used to examine the alkali-budgets of concrete (Table 5). Likewise, the ratio of water-soluble alkali versus total alkali content (Na<sub>2</sub>Oeq) of the cement, found to be 0.74 (rounded as 0.7), will be used for the estimation of water-soluble alkali of cement.

#### 3.3 Concrete

#### Dedolomitization and sol/gel exudation

Reaction rim developed on the dolomitic limestone coarse aggregate undergoing dedolomitization (Figures 2a,e). Under SEM, reacted dolomite rhombohedra presented a mottled appearance of brucite and calcite, leaving a pseudomorphic texture (Figures 2d,h). At the cement-aggregate interface, hydrotalcite-like material occurred absorbing Al ions from cement paste (Figure 2d). Carbonate halo dominated by calcite appeared in the cement paste surrounding the dedolomitized aggregate (Figures 2b,f). Just outside the carbonate halo, siliceous halo with a wet appearance occurred (Figure 2a,c,e). This was a water-soluble sol/gel-like material containing small amounts of alkali with [Ca/Si] atomic ratio around 1.2, which is intermediate between typical ASR gel and CSH gel indicative of a pozzolanic reaction. Cryptocrystalline quartz in the dolomitic aggregate has been converted to a gel, while brucite mostly to Mg-silicate gel (SiO<sub>2</sub>20-30%, MgO 5-20%, CaO 20%, and K<sub>2</sub>O <2%). Cracking of concrete was often stopped at the dolomitic aggregate-paste interface, suggesting the cracks are shrinkage crack of paste (Figure 2g).

#### Debonding, delamination and repair works

Debonding of concrete occurred at the interface between the dolomitic limestone coarse aggregate and cement paste around steel reinforcing bars (Figure 3a), leaving molds and casts of the coarse aggregate with a film of calcite powders and air voids (Figures 3b,c). The underlying concrete was porous with a honeycomb structure presenting a white carbonated appearance. Cosmetic mortar layer, usually covered to hide the rough surface and porous structure of concrete, was delaminated in places (Figures 3a,d), and vertical cracks appeared on the surface narrowing toward the bottom (Figure 3e). Limestone dust used as sand exhibited pronounced dedolomitization rims without cracking, but it was only clayey carbonate particles that produced open cracks. Cement paste on the mold of the aggregate was highly carbonated, suggestive of the presence of a water membrane during the masonry work. Repair concrete for patch work was well-bonded to the underlying concrete but the latter retains numerous cracks formed by the chipping (Figures 3a,f,g). Repair mortar was patched up on concrete with intense carbonation

(Figures 3a, 4a,b), a result of long exposure to the atmosphere and frequent drying/wetting of sprayed water during the repair work. The age of the concrete/repair mortar was 6 months at the time of evaluation.

#### 3.4 Alkali budgets in concrete

The estimated alkali content of the Portland cement, based on EDS analysis of unhydrated cement particles in concrete along with the designed mix (450kg/m<sup>3</sup>) in construction records, ranged between Na<sub>2</sub>Oeq 0.46-0.64%, corresponding to Na<sub>2</sub>Oeq 2.1-2.9kg/m<sup>3</sup> of concrete (Table 5). However, the total available alkali in concrete (i.e. total cement alkali + water soluble alkali of coarse and fine aggregates + other releasable alkali) amounted to Na<sub>2</sub>Oeq 3.0-3.4 kg/m<sup>3</sup>. This was based on EDS analysis with wet chemical analyses of water-soluble alkali of concrete currently adopted in Japan (40°C, <0.3mm, solid: water =1:10, shaking 30 minutes, General Project Method [3]), coarse aggregate (both the unused and the extracted from concrete), and unused fine aggregate. The above alkali level is marginal to promote alkali-aggregate reaction for typical ASR aggregates in concrete. However, this level of alkalis is sufficient to create deleterious expansion in concrete incorporating typical ACR aggregate from Kingston, Canada and highly reactive ASR aggregate (e.g. opal) present in the pessimum proportion [1]). It is interesting to note that the dolomitic limestone coarse aggregate, characterized by the conspicuous reaction rims and extracted from the concrete, contained nearly Na<sub>2</sub>Oeq 1.0 kg/m<sup>3</sup> of water-soluble alkali, some of which was possibly absorbed from surrounding cement paste in concrete.

#### 3.5 Expansion tests

In the accelerated expansion tests, dolomitic limestone aggregate produced non-deleterious degrees of expansion as to ASR (0.032% at 14 days) with RILEM AAR-2 (e.g. ASTM C1260 < 0.1% at 14 days), as well as to ACR (0.040% at 28 days) with RILEM AAR-5 test (< 0.1% at 28 days [4]) (Figure 1). Concrete core specimens from both sound and cracked concretes produced marginal expansion (0.095% at 21 days), according to the accelerated concrete core expansion test developed by Katayama et al. for ASR (deleterious expansion: >0.1% at 21 days [2]), along with radial expansion cracks filled with ASR gel (Figures 4c,d,e). ASR gel in the dolomitic aggregate, derived from cryptocrystalline quartz and forming veins (Figure 4f) was generally Ca-rich (SiO<sub>2</sub> 40%, CaO 20%, Na<sub>2</sub>O 5%, and K<sub>2</sub>O <1%) and has been crystallized into rosette-like aggregation. Dedolomitization proceeded on the periphery of the aggregate, brucite and cryptocrystalline quartz had mostly been converted to spots of Mg-silicate gel rich in Ca (SiO<sub>2</sub> 15-20%, MgO 15%, CaO 20%, Na<sub>2</sub>O 1%, and K<sub>2</sub>O <1%).

#### 4 DISCUSSION

# 4.1 Dedolomitization, alkali-silica reaction and pozzolanic reaction

Rim-formation of dolomitic aggregates has been reported from Iowa, USA, but this was not related to deterioration of concrete [5]. In Saudi Arabia, no evidence has been detected that dedolomitized aggregate with distinctive rims had produced expansion cracks, with or without sol/like exudation. Hence, neither the dedolomitization nor the alkali-silica reaction has the expansive nature, and deleteriously expansive alkali-carbonate reaction did not occur in these concretes, unlike the Canadian cases [1]. It is unlikely that ASR took place in field concretes, because cryptocrystalline quartz in the dolomitic aggregate was very scarce (only 1%), and the alkali level of the concretes is marginal to cause ASR. The dark sol/gel surrounding the dolomitic aggregate is a product of harmless "pozzolanic reaction", with an intermediate composition between typical ASR gel and cement hydrates CSH gel. This was formed through an interaction between cement paste and siliceous sol/gel, derived either from ASR gel or decomposed CSH gel during the formation of carbonate halo that replaces CSH gel [1]. This type of sol-exudation from dolomitic aggregate was first illustrated here in the freshly sampled concretes.

#### 4.2 Debonding of aggregate, cracking and early removal of concrete forms

Construction records indicate that the limestone coarse aggregate was mostly used unwashed. According to Maslehuddin et al. [6], debonding of aggregate occurs when the content of limestone dust exceeds 5%. Coating of the limestone dusts on the coarse aggregate was responsible for the poor bonding at the aggregate-paste interface. The occurrence of the debonding of concrete around steel bars is related to the construction method which successively removes concrete forms in the consolidation period. Concrete forms were possibly planned to remove

one hour before the final setting of the cement paste at standard temperature (23°C, Table 2) accommodating to higher temperature (35°C) typical of the region. However, it is conceivable that much higher temperature of the concrete forms by the sunshine accelerated the hardening of fresh concrete and adhesion to the forms. It is very likely that this retarded the demolding process by the friction caused and produced a shear stress around the steel bars, thus promoting debonding of the concrete cover around the porous honeycomb structure. Deep vertical cracking is probably a drying shrinkage, formed by insufficient curing of concrete, although a curing agent was used.

#### 4.3 Honeycomb, delamination and repair works

The formation of honeycomb structure around the reinforcing steel bars lies in the poor workmanship (Table 6). High content of free-lime in the cement might have affected the workability producing a stiffening nature and a porous structure. The cracking of the cosmetic mortar on the concrete wall is drying shrinkage, due possibly to high water ratio applied to improve the workability of fresh mortar containing limestone dusts in the masonry work. The delamination of this cosmetic mortar layer was enhanced by the poor removal of underlying honeycombs and insufficient filling. Patching materials often produced weak bond to concrete by a water membrane formed by the over-wetting. Intensive chipping of such porous concrete damaged the underlying sound concrete, producing numerous microcracks.

## 5 CONCLUSIONS

• Dolomitic limestone produced conspicuous reaction rim and carbonate halo due to dedolomitization in the concrete walls, but this reaction did not accompany expansion cracks around the aggregate. This aggregate tested as innocuous according to RILEM AAR-2 and AAR-5. Free-silica content in the coarse aggregate was too small (only 1%) to cause expansive alkali-silica reaction (ASR) in concrete under normal conditions. Thus, deleteriously expansive, so-called alkali-carbonate reaction (ACR) did not take place.

• The concrete wall contained estimated alkali Na<sub>2</sub>Oeq 0.46-0.64% based on EDS analysis, corresponding to Na<sub>2</sub>Oeq 2.1-2.9 kg/m<sup>3</sup>. The total available alkali inclusive of the contribution from the aggregates in concrete was Na<sub>2</sub>Oeq 3.0-3.4 kg/m<sup>3</sup>, marginal to promote ASR in concrete. In general, this level of alkalis is sufficient for ACR or a particular ASR at pessimum proportion to develop expansion. In the case examined here, ASR may develop in the long term, only when high temperature or external alkali will be supplied with much moisture.

• The cracking, delamination and debonding of the concrete are due to poor workmanship during concrete casting, preceded by the careless use of unwashed coarse aggregate covered with limestone dusts and followed by the inappropriate demolding of the concrete forms, superimposed finally by poor repair work at drying conditions.

#### 6 REFERENCES

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Т	TABLE1: Chemical compositions of crushed coarse aggregate (wt%)														
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	SO3	P <sub>2</sub> O <sub>5</sub>	$\rm H_2O^+$	CO <sub>2</sub>	Insol.	Total	f.SiO <sub>2</sub>	H <sub>2</sub> O-
1	1.48	0.17	0.18	8.21	42.74	0.05	0.05	0.16	0.01	0.76	42.48	2.86	99.15	1.0	0.49
2	1.51	0.15	0.14	5.37	46.09	0.05	0.06	0.14	0.01	0.77	41.85	3.19	99.33	0.8	0.87
A	Analysis: on dry basis (105 °C)														
1:	1: milky-white: dolomitic limestone; dolomite = $40.2\%$ , calcite = $59.8\%$														

2: light gray: dolomitic limestone; dolomite = 26.3%, calcite = 73.7%

Dolomite percentage in the carbonate fraction (d) was calculated after Katayama [7]

d = 56.03 x 100/(21.86m + 25.62), where m = CaO/MgO

TAB	TABLE 2: Chemical compositions of cement and clinker (wt%)																	
	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	SO3	$P_2O_5$	Cl	Ig.loss	Insol	Total	f.CaO	$\rm CO_2$	Na2Oeq
cement	19.11	0.31	4.34	3.41	0.04	3.04	60.92	0.15	0.71	2.64	0.07	0.01	4.11	0.71	99.57	1.40	3.21	0.62
clinker	20.49	0.41	5.69	3.84	0.04	2.53	64.42	0.15	0.90	0.88	0.07	0.01	0.24	0.12	99.79	2.70	0.05	0.74
Ratio*	0.93		0.76	0.89														
	Calculated phase compositions											Setting time (23°C)						
	alite	belite	alumin	ferrite	f-CaO	arca	gyp	calcite	total	LSF		Water	W/C	Initial	Final			
			ate			nite	sum					(ml)	(%)	hr:min	hr:min			
cement	41.0	23.9	5.7	10.3	1.4	0.9	4.0	7.3	94.5			165.5	25.5	2:20	3:27			
clinker	51.8	19.8	8.6	11.7	2.7	1.2			95.8	0.968								
**	62.8	11.4	8.6	11.7	0.0	1.2			95.8	0.968								
* The	ratio of	dilutio	n of clin	nker into	cement	t, with a	verage c	of 0.86.										

Equivalent alkali Na<sub>2</sub>Oeq = Na<sub>2</sub>O + 0.658K<sub>2</sub>O \*\* If free-lime = 0%, alite content will be 62.8%

Lime saturation factor (LSF) = $100CaO/(2.80SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3)$ 

TABLE 3: Total alkali and water-soluble alkali of cement by wet-chemical analysis (wt%)													
			Clin	nker		Cement							
		measured	1		estimated			measured	1	estimated			
	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> Oeq	Na <sub>2</sub> O <sub>n</sub>	Na <sub>2</sub> Os	Ratio	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> Oeq	Na <sub>2</sub> O <sub>n</sub>	Na <sub>2</sub> O <sub>s</sub>	Ratio	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	
Dry	0.15	0.90	0.74	0.15	0.44	2.47*	0.15	0.71	0.62	0.15	0.32	2.07**	
Water-sol.							0.082	0.574	0.460				
Ratio							0.55	0.81	0.74***				

\* Total alkali of clinker=(6) x [(1)+(4)] =2.47 x [(1)+(4)] ~ 2.47 x (minimum alkali of clinker Na<sub>2</sub>Oeq (1) of TABLE 5), the ratio 2.47 may not be stable (too little Na<sub>2</sub>O, the same as that of the cement) and hence rejected

\*\* adopted as 2.0, total alkali of cement =(12) x [(7)+(10)]=2.07 x [(7)+(10)] ~ 2.0\* x (minimum clinker alkali Na2Oeq (1) of TABLE 5)

\*\*\* adopted as 0.7 Water-soluble alkali of cement = 0.74 x total alkali of cement (9) ~ 0.7\*\* x (total alkali of cement (3) of TABLE 5)

(1): Assumption: Na2O is present as non-sulfates, partly water-soluble (retainable in hardened concrete for EDS analysis)

(2): Assumption: mostly derived from alkali sulfates, e.g. arcanite K<sub>2</sub>SO<sub>4</sub>

 $(3)(9): Na_2Oeq = Na_2O + 0.658K_2O$ 

(4):  $K_2O$  in non-sulfates expressed as  $Na_2Oeq = (1)$  (Assumption:  $Na_2O$ :  $K_2O$  molar ratio = 1:1) This  $Na_2On$  is partly water-soluble (5):  $K_2O$  in sulfates = (3) - (1) - (4) Assumption: this  $K_2O$ , expressed as  $Na_2Os$ , is water-soluble (not retainable in hardened concrete) (6): Ratio = (3)/[(1)+(4)] to estimate total  $Na_2Oeq$ , based on total  $Na_2Oeq$  of non-sulfates in clinker (retainable in hardened concrete)

(7): Assumption: all Na2O is present as non-sulfates, partly water-soluble (retainable in hardened concrete)

(8): K2O of cement. Assumption: mostly derived from alkali sulfates, e.g. arcanite K2SO4

(10): K<sub>2</sub>O in non-sulfates = (7) (Assumption: Na<sub>2</sub>O: K<sub>2</sub>O molar ratio = 1:1) This Na<sub>2</sub>On is partly water-soluble (retainable in concrete) (11): K<sub>2</sub>O in alkali sulfates = (9) - (7) - (10) Assumption: this K<sub>2</sub>O, expressed as Na<sub>2</sub>Os, is water-soluble (not retainable in concrete) (12): Ratio = (9)/[(7)+(10)] to estimate total Na<sub>2</sub>Oeq, based on total Na<sub>2</sub>Oeq of non-sulfates in cement (retainable in concrete)

TABLE 4: Minimum alkali content of cement clinker in the sound areas of concrete, representing different period of												
construction of a structure, by EDS analysis on polished thin section (wt%, average of two analyses for each phase)												
		K2	2(S4)			K2	(S5)			K2	(S8)	
	Alite	Belite	Alumi	Ferrite	Alite	Belite	Alumi	Ferrite	Alite	Belite	Alumi	Ferrite
			nate				nate				nate	
SiO <sub>2</sub>	24.70	31.55	5.49	5.23	25.27	31.94	6.84	5.49	24.42	30.98	6.47	5.54
TiO <sub>2</sub>	0.77	0.65	0.43	1.59	0.86	0.63	0.57	1.32	0.45	0.76	0.53	1.57
Al <sub>2</sub> O <sub>3</sub>	1.27	1.67	28.21	17.82	0.69	0.98	23.99	20.29	0.95	1.74	26.05	19.38
Fe <sub>2</sub> O <sub>3</sub>	0.86	1.15	4.40	21.51	0.66	0.89	8.53	19.70	0.52	1.44	4.56	20.31
MnO	0.03	0.05	0.07	0.44	0.00	0.00	0.04	0.05	0.05	0.36	0.07	0.25
MgO	1.52	0.72	0.25	2.71	1.33	0.01	3.06	2.26	0.84	0.17	0.19	2.56
CaO	66.62	60.10	53.87	45.06	67.49	60.35	48.33	45.18	67.61	59.47	55.74	45.78
Na <sub>2</sub> O	0.16	0.25	0.94	0.00	0.06	0.20	2.49	0.14	0.09	0.15	0.84	0.00
K <sub>2</sub> O	0.00	0.27	1.65	0.02	0.00	0.14	0.09	0.03	0.00	0.33	0.78	0.08
SO <sub>3</sub>	0.04	0.66	0.03	0.29	0.35	0.52	0.25	0.45	0.16	0.67	0.10	0.10
Total	95.76	97.05	95.33	94.65	96.74	95.67	94.16	94.88	95.08	96.05	95.30	96.32
Na <sub>2</sub> Oeq	0.16	0.43	2.03	0.01	0.06	0.30	2.55	0.16	0.09	0.37	1.35	0.05
Na2Oeq*	0.09	0.09	0.20	0.00	0.03	0.06	0.26	0.02	0.05	0.07	0.14	0.01
Total Na2Oeq		0	.38			0.	37			0.	27	
* in clinker,	assumpti	on: alite 55	%, belite 20	%, alumina	te 10%, fer	rite 10% (to	otal 95%), tł	ne remainin	g 5% (peric	lase, free-lir	ne) was om	itted

TABLE 5: Alkali budgets in concrete based on EDS analysis and wet chemical analysis (wt%)													
		Clir	nker			Cement					C.aggr		
	Minimum alkali To by EDS all			Total alkali	Total alkali	Total alkali	Water-so 1 alkali	,	Water-sol	uble alkali	Ĺ	Total ava alkali	Water-S alkali
	measured			estimated					meas	sured		estimated	
	%			%	6	kg/	kg/m <sup>3</sup>		%		kg/m <sup>3</sup>		$kg/m^3$
	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O <sub>eq</sub> (1)	Na <sub>2</sub> O <sub>eq</sub> (2)	Na <sub>2</sub> O <sub>eq</sub> (3)	Na <sub>2</sub> O <sub>eq</sub> (4)	Na <sub>2</sub> O <sub>eq</sub> (5)	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> Oeq (6)	Na <sub>2</sub> Oeq (7)	Na <sub>2</sub> Oeq (8)	Na <sub>2</sub> Oeq (8)
K2(S4)	0.23	0.22	0.38	0.76	0.64	2.87	2.01	0.036	0.107	0.106	2.29	3.35	0.76
K2(S5)	0.34	0.04	0.37	0.74	0.62	2.80	1.96	0.036	0.112	0.110	2.59	3.43	0.79
K2(S8)	0.17	0.15	0.27	0.54	0.46	2.06	1.44	0.032	0.108	0.103	2.42	3.04	0.89
	Coar	se aggreg	ate (separ	ated)	Coarse aggregate (unused)				d) Fine aggregate (unused)				
	,	Water-sol	uble alkal	i	Water-soluble alkali				Water-soluble alkali				Water-So alkali
		mea	isured		measured						est.		
		%		kg/m <sup>3</sup>		%		kg/m <sup>3</sup>		%		kg/m <sup>3</sup>	kg/m <sup>3</sup>
	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O <sub>eq</sub> (10)	Na <sub>2</sub> O <sub>eq</sub> (11)	Na <sub>2</sub> O <sub>eq</sub>	Na2Oeq	Na <sub>2</sub> O <sub>eq</sub> (12)	Na <sub>2</sub> O <sub>eq</sub> (13)	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> Oeq (14)	Na <sub>2</sub> Oeq (15)	Na2Oeq (8)
K2(S4)	0.031	0.121	0.111	1.02									0.15
K2(S5)	0.032	0.124	0.114	1.05	0.023	0.008	0.028	0.26	0.004	0.007	0.009	0.07	0.30
K2(S8)	0.035	0.137	0.125	115									0.65

(1)(6)(10)(12)(14): Na2Oeq=Na2O+0.658K2O (2): Total alkali of clinker=2.0\*x(1)

(3): Total alkali of cement =0.85x(2) = 0.85xclinker alkali=0.85x2.0\* minimum alkali by EDS (exclusive of alkali sulfate)=1.7x(1) (assumption: cement clinker was about 15% diluted when producing cement)

(4): Total alkali of cement in concrete=((3)/100)x450kg/m3 (construction record)

(5): Water-soluble alkali of cement in concrete=0.7\*\*x(4) \*\*see TABLE 3

(7):Water-soluble alkali in concrete=((6/100))x2350kg/m<sup>3</sup>

(8):Total available alkali in concrete=(4)+(13)+(15)+(16)=(4)+(7)-(5)

(9):Absorbed alkali in coarse aggregate=(11)-(13) Derived mainly from cement

(11):Absorbed alkali in coarse aggregate in concrete=((10)/100)x920kg/m3 (construction record)

(13):Water-soluble alkali of unused coarse aggregate in concrete=((12)/100)x920kg/m<sup>3</sup> (construction record)

(15):Water-soluble alkali of unused fine aggregate in concrete=((14)/100)x810kg/m3 (construction record)

(16):Total of released alkali from aggregates and admixture=(7)-(5)-(13)-(15)

TABLE 6:	Suggested ca	uses of obs	served defects	s in concrete	and in repair	materials			
$\land$		Defect	s in construc	tion work			Defects in	n repair work	
		Deb	onding		Cracking	Delami- nation	Unfilled vacancy	Cra	cking
	Cold joint	Honey-	Around	Coarse	Mostly	Interface	Interface	Toward	Surface of
		comb	depth of	aggregate	toward steel	with	with	bottom of	underlying
			steel bars		bars	concrete	concrete	mortar	concrete
	Hiatus	Poor	Rapid	Poor	Drying	Poor	Poor patch	Drying	Vigorous
	before next	vibration	hardening	bonding of	shrinkage	chipping of	up/padding	shrinkage	chipping
	placing of	of fresh	of surface	aggregate-	due to	porous	of viscous	due to high	of concrete in
	fresh	concrete	concrete by	mortar	shortage of	concrete	mortar in	water, with	repair work
	concrete	around	high	interface	curing		masonry	limestone	
		steel bars	temperature			Poor	work	dusts	
	Horizontal			Aggregate	Too fast	infilling of			
	debonding	Porous	Shear stress	coated with	removal of	repair		Penetrated	
	& cracks	structure	by removal	limestone	forms	mortar		within repair	
Suggested		often	of concrete	dusts used				mortar	
causes		developed	forms	unwashed	Vertical &	Poor			
		around	during		horizontal	bonding by			
		steel bars	consoli-		cracks*	water			
			dation			membrane			
						in masonry			
			Poor			work			
			bonding of						
			aggregate &						
			porous						
			structure						
Wall concrete	(x)	(x)	K2(B5)	K2(B5) C4(C30)	K2(C1)				
Cosmetic						K2(B15)		K2(B15)	
mortar						K2(D13)		C4(C30)	
Repair							$C1(\mathbb{R}^{23})$		
mortar							01(1025)		
Repair									K1(R24)
concrete									111(1127)
K1(R24): Re	paired; K2(B	5), K2(B15):	Bad location,:	K2(C1): Crae	ck area; C1(R	23): Repaired;	C4(C30): Cra	cked area	

\* some vertical cracks may be thermal contraction crack, (x) not sampled for this investigation



FIGURE 1: Accelerated expansion tests of aggregate and concrete: (a) RILEM AAR-2 mortar bar and AAR-5 concrete microbar of dolomitic limestone coarse aggregate; (b) Concrete core expansion test for samples from cracked area (C4(C30)) and sound area (K4(S60)) of concrete structures. Criteria for deleterious expansion are >0.1% at 14 days for AAR-2 (ASTM C1260), at 28 days for AAR-5 [4] and at 21 days for concrete core [2].



FIGURE 2: (a)-(d) Sound (K2(S1)) and (e)-(h) cracked (K2(C1)) portions in one structure. (a): Siliceous exudation (dark) skirting the carbonate halo. (creamy) in cement paste, and reaction rim (buff-color) within aggregate. (b) Dedolomitization forming reaction rims (dark) and carbonate haloes (bright) on the coarse aggregate without cracking; (c) Siliceous exudations replacing CSH gel; (d) dedolomitized rhombohedra within reaction rim. (e) Siliceous rim on the dolomitic aggregate; (f) Dark reaction rims and carbonate haloes on the dolomitic aggregate; (g) Shrinkage crack in cement paste, (h) Mottlling by dodolomitization.



FIGURE 3': (a) Core samples showing, from left to right, debonding of cover (K2(B5)), delamination of cosmetic mortar on honeycomb (K2(B15)), patchwork of repair concrete (K1(R24)) and repair mortar (C1(R23)). (b) Debonding of concrete cover showing aggregate molds (c) with a film of limestone dusts on aggregate ((K2(B5))). (d) Cosmetic mortar layer delaminated at the smooth bottom surface, and (e) drying shrinkage crack from the mortar surface and dedolomitized fine aggregate (K2(B15)). (f) good boning of patch work concrete onto the underlying concrete, (g) which was cracked due to chipping (K1(R24)).



FIGURE 4': (a) Boundary of patch-up mortar with underlying concrete; (b) Carbonation of underlying concrete patched up with repair mortar (C1(R23)); (c) Accelerated concrete core expansion test (K4(S60)), producing faint radial cracks (d) in the dolomitic aggregate, (e) in the cement paste, and (f) veins filled with ASR gel in the aggregate; (g) Aluminate (low-alkali, cubic) and (h) alkali sulfate arcanite in the interstitial phases of cement clinker.